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Thermo chemical study on imidazolium bromide using ultrasonic velocity

Seethalakshmi.K*, Jasmine Vasantha Rani.E and Padmavathy.R

Department of Physics, Seethalakshmi Ramaswami College, Trichy-2, Tamilnadu.

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ABSTRACT

The study of liquid/solutions using acoustical methods constitutes the mining field for scientists. Compressibility measurements are highly accurate and yield interesting informations. The sign and magnitude of compressibility indicates the solvation effects. The structural changes in the primary and secondary regions are generally referred to as solvation. The thermochemical parameters have been proven to be a very useful tool in elucidating the structural interactions taking place in the solutions. In the present investigation, BMIMBr is dissolved in formamide and the fundamental quantities are measured in various molalities and the temperatures ranging from 278.15K to 328.15K. In the present study, the solvation of BMIMBr in non-aqueous medium is taken for interpreting the various interactions occuring between the solute and solvent and the effect of temperature and concentration on solvation is also analyzed.

Introduction

Ionic liquids (ILs) are compounds consisting of an organic cation with an organic or inorganic anion, with melting points below the boiling point of water [1]. ILs have unusual properties including non-volatility, non-flammability, high ionic density, conductivity, chemical and electrochemical stability, etc., They are gaining interest as alternatives to conventional molecular liquids [2-6]. In the present investigation, solvation effects of BMIMBr are studied in non-aqueous medium. By measuring the fundamental quantities such as density and ultrasonic velocity of BMIMBr in formamide from 278.15K to 328.15K at different concentration, the solvation number were computed. From the analysis of solvation, the imidazole salts in formamide reveals the structural interaction taking place in the solution.

Experimental

Here, 1-butyl-3-methyl imidazolium bromide and formamide are purchased from Sigma Aldrich chemicals, USA with high purity (99%) and hence used without any further purification. A solution of BMIMBr in formamide are prepared with five different molalities. Density of the solution is measured using 25 ml specific gravity bottle with an accuracy of 0.001gm/cc. The ultrasonic velocity is measured using Mittal's interferrometer, with an accuracy of $\pm$2 m/s.

Computation

Using the experimentally measured values, the following thermodynamical parameters are computed using the standard formulae[7]

(i) Internal Pressure and Free Volume:

$$\prod_i = bRT(k\eta/U)^{1/2} * (\rho^{2/3}/M_{eff}{}^{7/6}$$

$$V_f = (M_{eff} * U/k\eta)^{3/2} cc$$

(ii) Adiabatic compressibility:

$$\beta = \frac{1}{U^2\rho}\frac{cm^2}{dyne}.$$

(iii) Solvation Number:

$$n_h = \left(\frac{n_s}{n_i}\right)\left[1-\frac{\beta}{\beta_0}\right]$$

Where

R – gas constant(8.314×10^7)

T – temperature

b – cubic constant(2)

k – constant equal to 4.28×10^9

η – viscosity of the solution in poise

U – ultrasonic velocity in cm/sec

ρ - the density of the solution in gm/cc.

M_{eff} - Effective molecular weight of the solution in gm

β_0 & β - the compressibility of the solvent & solution in cm^2/dynes.

n_h, n_s & n_i are the primary solvation number, moles of solvent and moles of ions respectively.

Results and Discussion

Internal Pressure and Free Volume:

Internal pressure is a single factor which varies due to all the internal interactions. The variations of internal pressure and free volume with temperatures and molalities are shown in Figures 1 & 2 and the values are tabulated in Tables 1 & 2.From the figure, it is observed that the internal pressure increases with concentration. It exhibits a structure stabilizing nature. However, a dip in the increasing values of internal pressure with concentration is observed for BMIMBr (0.01m at 278.15K, 298.15K-328.15K) and (0.005m at 288.15K). This may be due to weakening of interactions at specific concentrations and temperature suggesting the loosening of structures due to lowering of cohesive energy. Figure 1.

Adiabatic compressibility:

The rise and fall is observed in adiabatic compressibility of BMIMBr. The values are reported in Table 3 and the graphical representations are shown in Figure 3.These rise and fall variations may support a strong asssociation taking place between the molecules of the solution.

Tele:

E-mail addresses: seethalakshmiramasamy@yahoo.in

Table- 1: Internal Pressure (atms)

Internal Pressure(Π_i)						
Molality (m)	278.15K	288.15K	298.15K	308.15K	318.15K	328.15K
0.001	18916.3	15971.9	13842.3	12762.2	11852.6	10794.6
0.005	19337.6	13829.9	14140.7	12836.6	11700.5	10965.3
0.01	16552.1	14487.3	12527.2	11775.6	11152.3	10059.8
0.015	18445.4	15898.2	13694.4	12443.7	11567.7	10593.9
0.02	18540.2	15919.7	13617.2	12457.0	11679.2	10571.2

Table- 2: Free Volume (cc)

Free Volume (V_f)						
Molality (m)	278.15K	288.15K	298.15K	308.15K	318.15K	328.15K
0.001	0.00909	0.016633	0.02800	0.03870	0.05243	0.07508
0.005	0.00850	0.025514	0.02605	0.03784	0.05448	0.07151
0.01	0.01352	0.022177	0.03755	0.04916	0.06268	0.09261
0.015	0.00974	0.016802	0.02878	0.04146	0.05614	0.07894
0.02	0.00952	0.016629	0.02914	0.04139	0.05449	0.07958

Table- 3: Adiabatic Compressibility

Adiabatic Compressibility x 10^{-11} (cm^2/dyne)						
Molality (m)	278.15K	288.15K	298.15K	308.15K	318.15K	328.15K
0.001	3.19	3.37	3.45	3.54	3.61	3.75
0.005	3.20	3.32	3.45	3.58	3.64	3.76
0.01	3.26	3.27	3.43	3.52	3.64	3.66
0.015	3.20	3.40	3.41	3.54	3.64	3.73
0.02	3.24	3.45	3.44	3.55	3.64	3.80

Table- 4: Solvation Number

Solvation Number (η_h)						
Molality (m)	278.15K	288.15K	298.15K	308.15K	318.15K	328.15K
0.001	352.2	-190.4	-289.2	83.8	543.0	425.6
0.005	51.2	16.7	-51.0	-29.3	75.7	73.5
0.01	-11.3	44.1	-10.3	24.6	35.8	95.1
0.015	17.8	-28.7	-0.4	9.5	25.4	35.9
0.02	2.7	-36.3	-8.3	3.3	19.0	5.9

Solvation Number:

Solvation Number of BMIMBr are reported in Table 4 and the variations are shown in figure 4. In the present study, the solvation number is computed from compressibility measurements. For (BMIMBr) above the room temperature (318.15K and 328.15K) the positive solvation number is observed. The variation in solvation number is observed only at lower concentration. As the temperature increased from 278.15K to 328.15K, the value of solvation number is decreased parabolically, from the positive high value and it increases above the room temperatures. The zero solvation number is found to be at higher concentration. These results suggests that the breaking of intermolecular H-bonding between adjacent molecules which disappeared in solution.

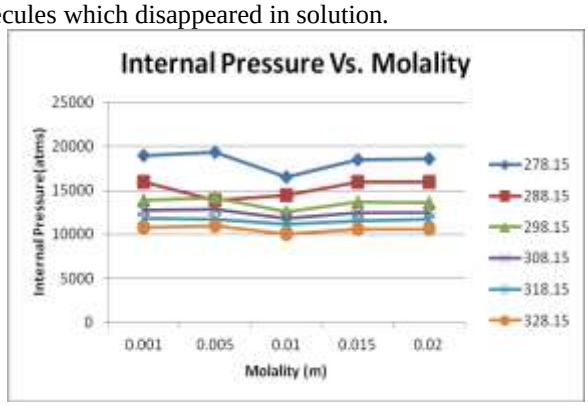

Fig. 1. Variations of internal pressure with temperatures and molalities

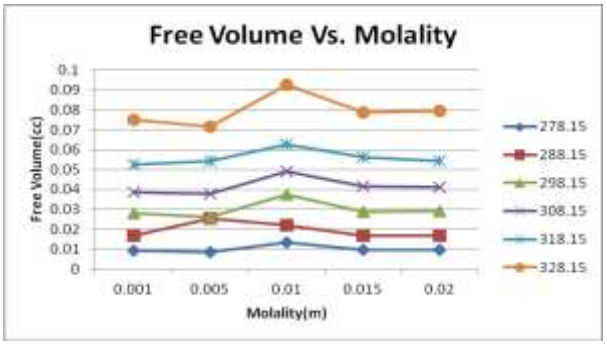

Fig. 2. Variations of free volume with temperatures and molalities

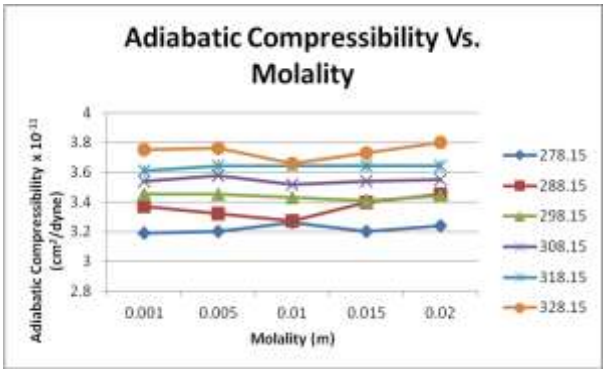

Fig. 3. Variations of adiabatic compressibility with temperatures and molalities

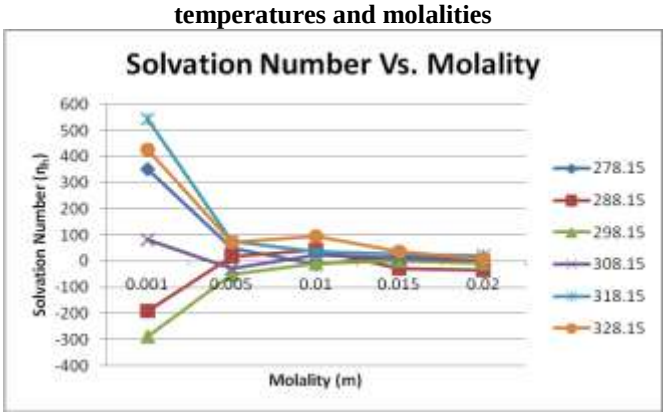

Fig.4. Variations of solvation number with temperatures and molalities

Conclusion:

In the present work, the acoustic studies are carried out to analyze the various molecular interactions occurring in the solution of BMIMBr.

From these graphs the following conclusions are drawn:

❖The internal pressure is found to decrease with concentration for the solution at 0.01m.This may be due to weakening of interactions at specific concentrations. This indicates reduction of cohesive forces as the molecules move away from each other with increase in temperature. The decreasing trend in internal pressure suggests that the solute has the tendency of breaking the structure of the solvent.

❖The free volume is found to increase with temperature. When the temperature is increased there is a tendency for the molecules to move away from each other which results in the reduction of cohesive forces and thus leading to an increase in free volume.

❖In BMIMBr, adiabatic compressibility shows decrease at lower molality and then it incrases at higher molality. It shows the breaking of H-bonds. These variations suggests that there is a strong solute-solvent interaction.

❖Compressibility method is used to study the solvation effect of the solution. The results indicate that solute-solvent binding is large with tertiary nitrogen of butyl group.

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